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Synthesis of an organic–inorganic hybrid material by solid state intercalation of 2-mercaptopyridine into Na-, Al(III)- and Co(II)-montmorillonite

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Abstract. **The preparation of an organic–inorganic hybrid material by solid state intercalation of 2-mercaptopyridine (2Mpy) into Na-, Co(II)- and Al(III)-montmorillonite has been studied using a variety of techniques. The extension of d_{001} from XRD proves that the intercalation of 2-mercaptopyridine into Na-, Co(II)- and Al(III)-mont occurs at ambient temperature in 5 mn. When the intercalated samples were heated at different temperatures, we found that the d_{001} gave different values. For instance, for intercalated Al(III)- and Co(II)-, d_{001} remained unchanged for a temperature under 500°C. However, for intercalated Na-mont, it shifted to 14 Å for a temperature of 300°C, the washing of different samples with a methanol solution shifted the d_{001} of intercalated Na-mont to 14 Å. However, for intercalated Al(III) and Co(II), it did not change. This proves that in the case of Na-mont, the molecules of 2-mercaptopyridine interact with the clay through hydrogen bindings and physical interactions. However, for Al(III) and Co(II), it forms coordination linking and physical interaction. ^{13}C NMR and FTIR spectroscopy have been employed for the characterization of the intercalation compounds. Tautomeric equilibrium between thiol and thione species of 2-mercaptopyridine must be taken into account to explain the arrangement of molecular aggregates and their particular orientation in the interlayer space. The isotherm of adsorption–desorption of nitrogen and topographic AFM images prove that intercalation of 2Mpy is accompanied by a total blockage of clay porosity and an increase in roughness.**

Keywords. **Organic–inorganic hybrid materials; solid state intercalation; montmorillonite clay; 2-mercaptopyridine.**

1. Introduction

The construction of organic–inorganic nano structure materials is an important target of modern materials research. The purpose behind such research is to develop functional materials. The smectite group, which includes montmorillonite, has enjoyed wide attention due to its interesting adsorptive/intercalation and cation-exchange properties.

Organoclay has received widespread attention in a number of industrial sectors including waste treatment (Koh and Dixon 2001; Koskinen and Hermison 2001; Beall 2003; Grosman *et al* 2004) catalysis, and electrode-modifiers. The synthesis, characterization and properties of smectite–organic intercalation compounds have been reported extensively (Theng 1997). The process often used for the preparation of organoclay is an intercalation into the clay in suspension state. These reactions are characterized by long time treatment and excessive use of organic solvent. Therefore, it is interesting to develop and test another efficient process of preparation of organoclay.

A process, which is not very frequently used and which allows the possibility of preparing compounds which are not accessible from solutions (Patil *et al* 1984), is the so-called solid–solid reaction. The latter is a mechanochemical adsorption that occurs between powders in the solid state (Rothenberg *et al* 2001). Solid-state intercalation of organic guest species into layered vanadium phosphorus oxide (Yamamoto *et al* 2001), zeolites (Lázár *et al* 1994) and layered clay minerals (Yariv and Lapides 2000; Khaorapapong *et al* 2001, 2002; Landau *et al* 2002) have been reported as a way of utilizing host structures. Solid-state intercalation can be split into two stages: one is the diffusion of guest species from the outer surfaces of guest solids and the other is the penetration of the guest species into the interlayer spaces.

Intercalation of pyridine and related derivatives in clays has been widely studied for several decades (Sabah and Celik 2002). Their intercalation can be achieved from the neutral molecules by interaction of the pyridine ring with the interlayer cations through water bridges and it can

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*Author for correspondence (bekrimene@gmail.com) also be achieved by cation exchange from the corresponding protonated (pyridinium) derivatives. What is interesting is the fact that intercalated pyridines can adopt different orientations in the interlayer space depending on both the structure of such molecules and the nature of the interlayer cation.

We report here the intercalation of 2-mercaptopyridine (2Mpy, figure 1) into Na-, Co(II)- and Al(III)-montmorillonite by solid–solid reaction. We have chosen this organic molecule for two principal reasons: (i) it is an interesting derivative of pyridine which contains functional groups (thiolate-S and aromatic-N) and therefore, it may interact with clay in different orientations and configurations, and (ii) it has the ability to both chelate and bridge transition metals.

We have characterized the intercalated products by X-ray diffraction (XRD), atomic force microscopy (AFM), infrared spectroscopy (FTIR), azote adsorption–desorption and thermo XRD.

2. Materials and methods

Montmorillonite clay was obtained from the region of Zaghouan, from the East West of Tunisia. The presence of smectite was confirmed by the d_{001} spacing of the sample after air drying, calcinations at 600°C for 2 h and glycol treatment. It was studied by El Hechi *et al* (2003) and Ayari *et al* (2004). In this study, we have shown that used smectite was essentially dioctahedral. By means of specific tests (test of lithium), it was found that it constitutes essentially of montmorillonite. Montmorillonites saturated with Na^+, Co^{2+} and Al^{3+} were prepared by suspending 5 g of purified smectite in 200 ml of freshly prepared 1M aqueous solution of the respective chloride salt (Cl_3Al and Cl_2Co were purchased from Aldrich), and changing each solution after 24 h. After 7 days of shaking, the clay was washed several times with distilled water until it was free of chloride (examined by $AgNO_3$ solution). The amounts of Na, Al and Co were determined after exchanging samples with the complex of ethylenediamine of copper (Bergaya 1997), and were respectively 101, 103 and 105 meq/100 g of Na-, Al- and Co-clay. 2-Mercaptopyridine was purchased from Aldrich.

The resulting intercalation materials were characterized by chemical analysis (Perkin-Elmer 2400 CHN analyser). The IR spectra were obtained with a Nicolet spectrophotometer (model 560) with a scanning range between 400 and 4000 cm^{-1}. The samples were prepared as tablets diluted in KBr while we kept constant the sample/KBr ratio and the total weight of sample. The 75 MHz ^{13}C solid-state NMR experiments were carried out with a BRUKER spectrometer (300 MHz).

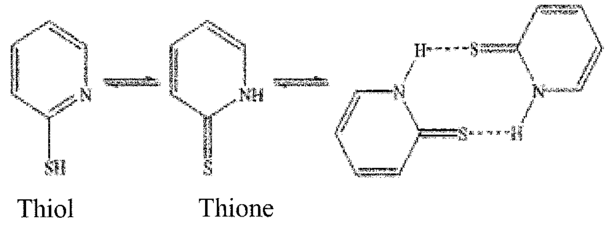

Figure 1. Chemical structure of 2-mercaptopyridine.

The surface roughness was checked before and after the intercalation process by topological images obtained by AFM.

AFM images were recorded on a nanoscope II instrument in contact mode and in a region of 500×500 nm^2 with a scan rate of 1 Hz at 256×256 resolution, for sample preparation for AFM analysis. We used the method of Occelli *et al* (2000). Wafers were formed by pressing powders of samples at about 15,000 kPa and were glued onto steel disks with epoxy resin and when the glue had dried, the atomic force microscope tip was carefully guided to the middle of the wafer thus beginning the analysis.

The RMS roughness was calculated from the following equation:

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{N} (z_i - z_a)^2}{N-1}}. \qquad (1)$$

In this equation, z_i is the image height at pixel i, z_a the average height and N the number of pixels in the AFM image. The interlayer space of organoclay was checked by XRD technique on a Panalytical diffractometer using Cu radiation. Nitrogen sorption isotherms were obtained with a Quantachrome instrument (Autosorb), prior to the analysis, the samples were outgassed in vacuum at 100°C for 2 h. BET surface areas were calculated from isotherm at relative pressures ranging from 0·05–0·30 (Brunauer *et al* 1938).

The t-method of Halsey (1948) was used for the determination of micropore volume in the presence of mesopores. This technique involves the measurement of nitrogen adsorbed by the sample at various low pressure values.

The intercalation of 2Mpy into Al-, Co- and Na-montmorillonite was achieved via solid–solid reactions. The mixtures of the hosts and the guest species were ground manually using an agate mortar and pestle at room temperature for 5 min. The molar ratio of 2Mpy to the interlayer Na, Co, Al cation was 3 : 1. When the solid–solid reactions were achieved, the intercalation compounds were washed repeatedly with *n*-heptane in order to remove excess of 2Mpy.

3. Results and discussion

3.1 *Spectroscopic studies*

Due to its structure (heterogeneous cyclic structure and the presence of mobile hydrogen), 2-mercaptopyridine molecules coexist in two tautomeric forms, thione and thiol (figure 1).

The predominance of a tautomeric form up to the other depends on many factors such as state of molecule (gaseous, solid), polarity of solvent and even temperature and pH solution.

It is well known that in solid state 2Mpy predominates in its thione tautomer conformation, forming molecular aggregates that are organized as dimmers through hydrogen bonding interactions (Zhang *et al* 2003) (figure 1). In order to determine the tautomeric form adopted by 2Mpy molecules after reaction with clay, IR and ^{13}C spectroscopy have been used.

Figure 2 shows the IR spectra of the starting mercaptopyridine, pure clay and Na-, Co-, Al-montmorillonite treated with 2Mpy. Their assignment of vibrational modes is represented in table 1.

The bands of 2Mpy have been assigned by means of theoretical calculation considering their thiol–thione tautomeric forms (Zhang *et al* 2003). The characteristic IR bands observed in the spectrum of pure 2Mpy (figure 2b) agree well with the theoretical bands predicted for 2Mpy in their thione form. However, after intercalation into Co and Al-montmorillonite, the characteristic bands of the thione form (1628, 1371, 732 cm^{-1} for Co-mont and 1628, 1370, 730 cm^{-1} for Al-mont) are observed in addition to the thiol bands (1452, 1421 and 761 cm^{-1} for intercalated Al-mont compound and 1448, 1421 and 757 cm^{-1} for Co-intercalated compound). Moreover, the band at 1582 cm^{-1} that is predicted in the thiol form, corresponding to stretching vibrations of the pyridine ring and to –SH bending, appears in Al-mont and Co-mont as a strong band at 1579 cm^{-1} for intercalated Co-mont and at 1575 cm^{-1} for intercalated Al-mont. For intercalated Na-mont, we observe only the characteristic bands of the thiol form. It is interesting to note that in the case of Co- and Al-mont, ν OH bands of water molecules (at 3438 cm^{-1}) and δ OH (at 1640 cm^{-1}) initially present in the interlayer space of the clay disappeared in the spectrum (figures 2d, e) indicating that the intercalation of 2Mpy thiol–thione replaces these water molecules. However, in the case of Na-mont these bands increase in area which indicates that intercalated Na-mont adsorbs water. From these results, we can assume that 2Mpy interacts with Al-, Co-mont in a different way from that of intercalated Na-mont. In the case of Co- and Al-mont, it is obvious that 2Mpy molecules take the place of water and interact directly with Co^{2+} and Al^{3+} cations. From FTIR study, we cannot deduce that 2 Mpy forms coordination linking with Co^{2+} and Al^{3+} because metal–sulfur bonds are located at wavelengths below the Nicolet 560 FT–IR series spectrometer's detection limit of 400 cm^{-1}. For intercalated Na-mont, we observe an increase of the intensity of water bands, probably the mode of interaction in this case is not the same, H_2O coexists with 2Mpy molecules and forms hydrogen linking with S–H of the thiol form. The increased water adsorption is due to grinding of mixture which is carried out in atmospheric ambient and in an open system.

Due to the complexity of ^{13}C NMR spectra when tautomeric species coexist, it has been necessary to use theoretical models based on spectroscopic simulation tools (Montserrat *et al* 2005).

The ^{13}C NMR spectrum of pure 2Mpy (figure a) shows well defined signals at 180, 149, 133 and 118 ppm, assignable to C2*, C6*, C3* and C5* carbon of the thione tautomer. The ^{13}C NMR spectrum of the intercalated Na-montmorillonite presents the signals of the thiol tautomeric form (153, 122 ppm) (figure 3c). These signals can be assigned to C2, C5 and C6.

For Al-mont and Co-mont intercalated samples, we observe signals which can be assigned to thiol and thione form, evidencing in this case the coexistence of both tautomeric species (thiol and thione). These results are in agreement with the IR spectroscopic results.

3.2 *Thermal analysis (thermo-XRD)*

The XRD patterns along with basal spacing (d_{001}) data of the intercalated 2 Mpy-mont composites are shown in figure 4. It reveals that d_{001} is about 19·1 Å for Na-intercalated sample, taking into account the thickness of the silicate layer (about 9·6 Å), and the thickness of mercaptopyridine molecules, a Δd_L value of 3·2 Å (Montserrat *et al* 2005). The increase of the interlayer distance for this compound is calculated from the corresponding d_{001} space. We have found that this value corresponds to the thickness of three layers of 2Mpy molecules disposed with the ring parallel to the plane defined by the silicate layers, for intercalated Co-mont and Al-mont, the basal spacing is about ~15 Å for the two compounds, which supposes that in these cases 2Mpy molecules take the same configuration which is different from that of intercalated Na-mont compound.

It is interesting to note that the washing of intercalated Na-mont with methanol decreases the d_{001} to 13 Å, however, for Co- and Al-mont, it did not change the d_{001}, which proves that in the case of Co- and Al-mont, 2Mpy molecules form with Al- and Co-mont a configuration more stable than that of Na-mont, probably they form coordination bonds.

In order to evaluate the mode of interaction with the intercalated sample, we have heated different compounds in temperatures ranging from 300–650°C. The heating of different intercalated compounds proves this suggestion.

The d_{001} of unheated Na-mont intercalated compound is about 19 Å, this trilayer intercalated compound is not stable by heating at a temperature of 300°C for 2 h, d_{001} decreases to 14·2 Å, which corresponds to a monolayer arrangement, therefore, the first two layers are less stable than the third one. This value is unstable under a temperature of 400°C, it shifts to about 12 Å, the IR spectra of intercalated Na-mont (not shown) heated at 300°C shows

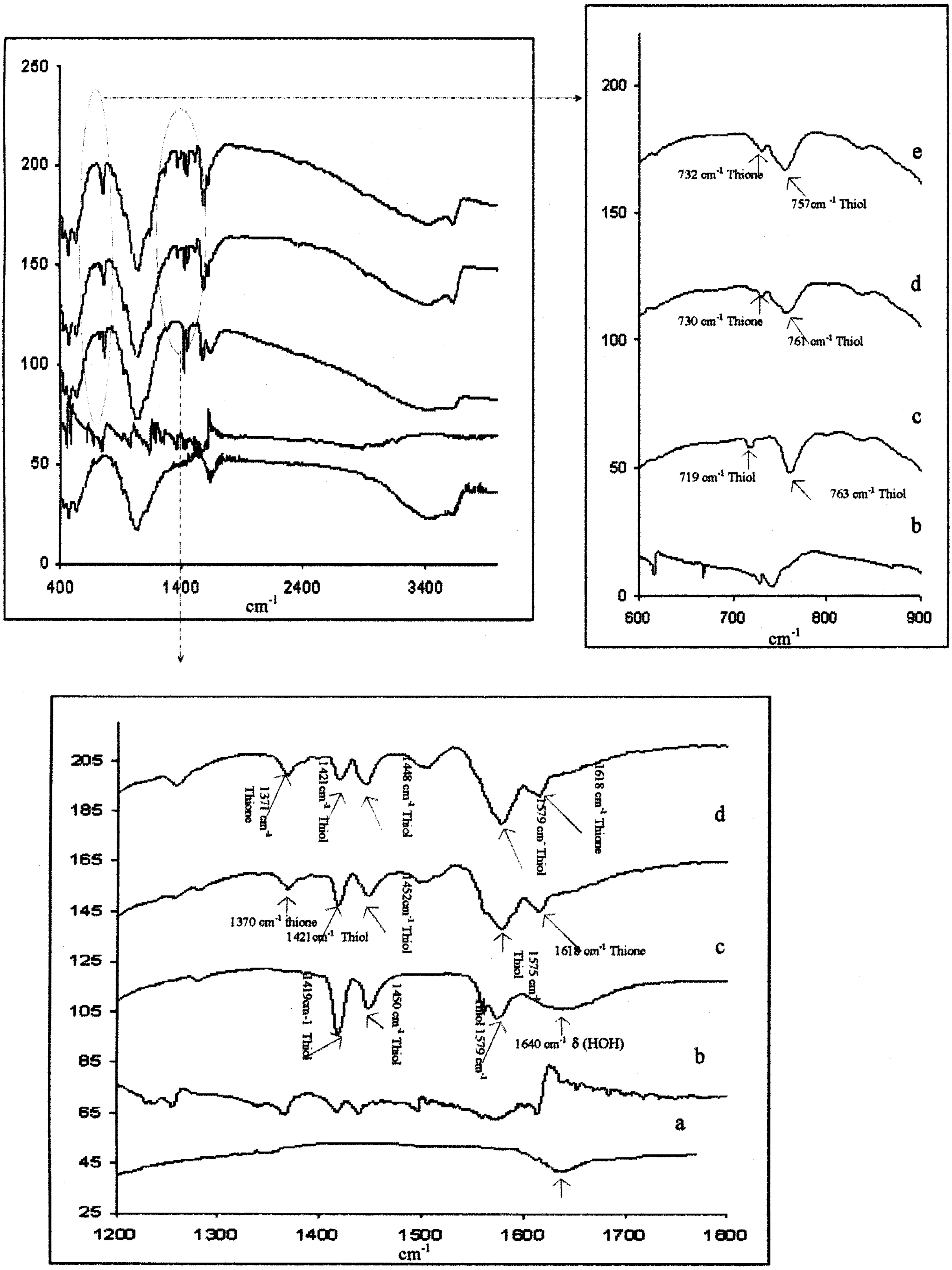

Figure 2. IR spectra (4000–400 cm^{-1} region) of (a) pure clay, (b) pure 2Mpy, (c) 2Mpy intercalated in Na-montmorillonite, (d) 2Mpy intercalated in Al-montmorillonite, (e) 2Mpy intercalated in Co-montmorillonite; the right spectrum represents a magnification in the 600–900 cm^{-1} region and the down spectrum represents a magnification in 1200–1600 cm^{-1} region.

Table 1. Frequencies (cm^{-1}) and assignment of vibrational modes in IR spectrum of 2Mpy molecule in its thiol–thione tautomeric forms† and corresponding frequency of composites.

2Mpy pure solid	2Mpy Na-mont	2Mpy Al-mont	2Mpy Co-mont	2Mpy-thione* (calcd)	Assignment	2Mpy-thiol* (calcd)	Assignment
1614	–	1628	1628	1641	ν_{8b}	1601	ν_{8b}
	1579	1575	1579			1582	ν_{8b}, δ_{CSH}
1576		1569	1569	1569	ν_{8a}, δ_{CNH}		
1441	1450	1452	1448	1467	ν_{19a}, δ_{CNH}	1461	ν_{14}
	1419	1421	1421			1416	ν_{19b}
1369	–	1370	1371	1345	ν_3		
743	763	761	757			764	δ_{10b}
	–	730	732	733	ν_{11}, $\delta_{CNH(\text{out of plane})}$		

*The assignment of the vibrational modes is taken from the normal mode assignment of benzene (Zhang *et al* 2003); †all the frequencies are expressed in wave numbers.

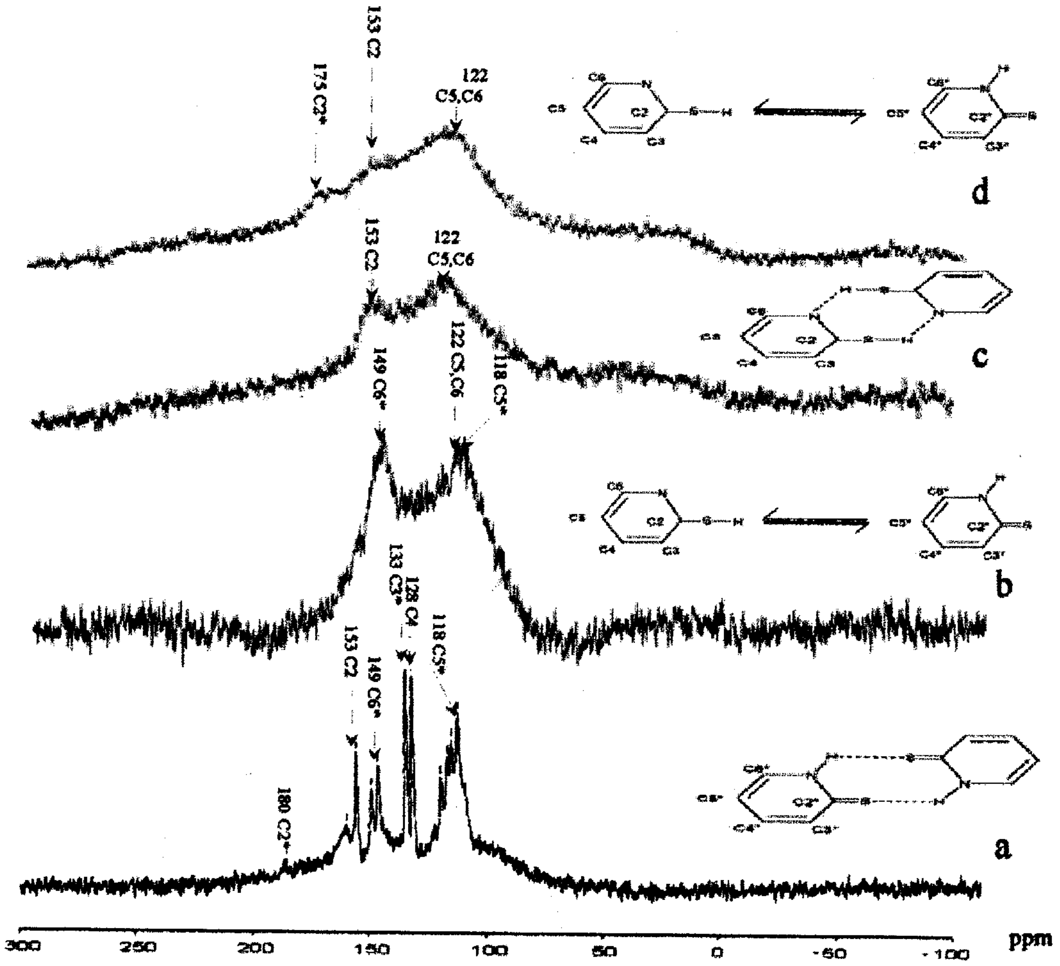

Figure 3. ^{13}C NMR spectra of (a) pure 2Mpy, (b) Al-montmorillonite treated with 2Mpy, (c) Na-montmorillonite treated with 2Mpy and (d) Co-montmorillonite treated with 2Mpy.

the coexistence of some peaks of 2MPy, for the sample heated at 400°C, it did not show any peaks of 2Mpy. Up to 550, d_{001} decreases to 10 Å confirming completely collapsed structure of montmorillonite. However, in the case of intercalated Al- and Co-montmorillonite compound, the d_{001} are stable under a temperature of 500°C; upon further heating up to 650°C, the d_{001} reflection shows a value of 10 Å, confirming a completely collapsed structure of montmorillonite. These results prove that in the case of intercalated Al- and Co-mont, molecules of 2Mpy form

Table 2. Chemical compositions of the products.

Intercalated compound	C (molar %)	N (molar %)	H (molar %)	C : H	C : N
Intercalated Na-mont	1·5	0·278	1·4	4.86	1
Intercalated Co-mont	0·76	0·14	0·75	4·95	1
Intercalated Al-mont	0·5	0·1	1·6	4·85	1

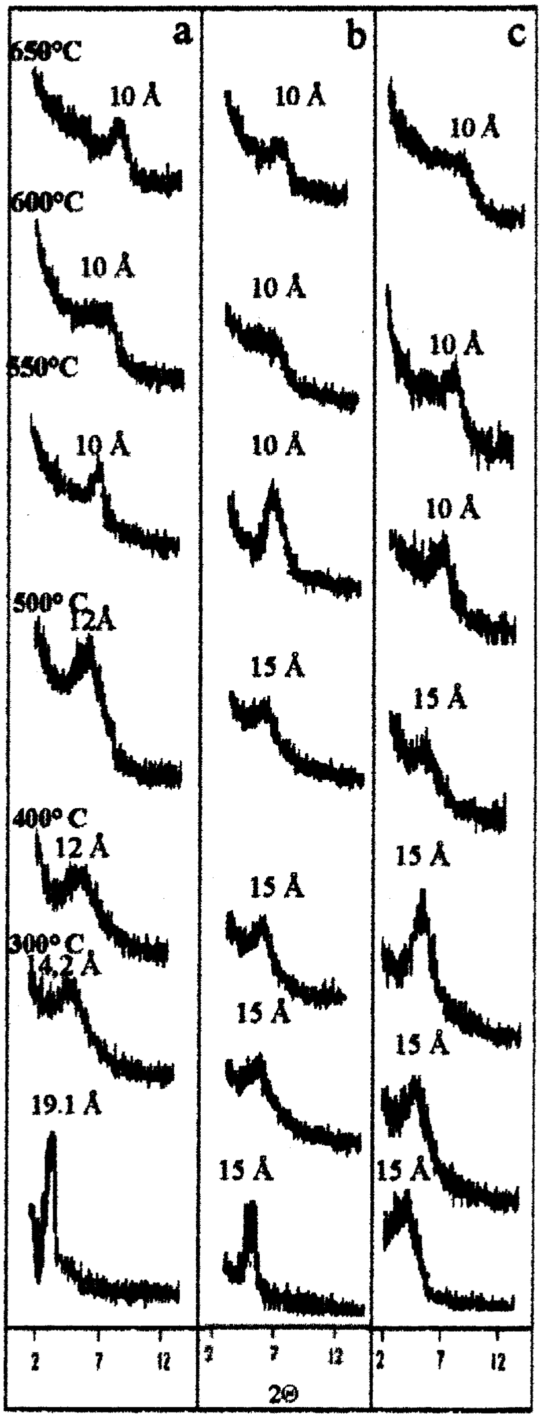

Figure 4. X-ray diffraction patterns and basal spacing (d_{001}) of intercalated composites heated at different temperatures for 2 h in air atmosphere.

coordinating links with Al and Co cations, however, for intercalated Na-mont, the S–H of the thiol interacts with H_2O by hydrogen interactions.

3.3 *CHN analysis*

In table 2, we represent the CHN molar composition of different intercalated compounds. From these values, we can deduce that the C : N : H ratio of the product is in good agreement with that of the 2Mpy molecule which proves the non-degradation of 2Mpy. The ratio of adsorbed 2Mpy to interlayer Na, Co, Al cations was estimated to be ~3 : 1, based on C content.

3.4 *Textural study*

Figure 5 represents the nitrogen adsorption–desorption isotherm of the samples, following the classification of BDDT (Deming *et al* 2004), all the adsorption isotherms are of type II, this type of isotherm represents unrestricted monolayer–multilayer adsorption, point B which represents the start of the linear central section of the isotherm, is usually taken to indicate the relative pressure at which monolayer coverage is complete.

For different samples, this value is about 0·4 P_0 (in our analysis P_0 is equal to ambient pressure). The Boer (De Boer 1958) hysteresis classification indicates that the hysteresis is of type B. We have selected Vt-method for microspores determination, the microspores of these samples are given in table 3, specific surface area is very low in all the intercalated solids, being between 4 and 15 m^2/g in most of them. This clearly indicates a total blockage of clay porosity by the intercalation of the organic molecules.

AFM images have been used by many researchers to characterize the morphology and roughness of materials such as polymeric membrane (Bowen and Donev 2000; Jones *et al* 2001; Ochoa *et al* 2001), inorganic materials such as alumina (Xu *et al* 2002), and clay minerals.

It was essentially limited for size characterization of clay particles (Plaschke *et al* 2001, 2002; Tounrassat *et al* 2003; Martinez *et al* 2004), but study of the morphology of organoclay by AFM images is not reported. AFM images were recorded for different samples and presented in figure 6. The RMS roughness was evaluated for each of the samples using (1). These results are represented in figure 6 and it ranged from 9·9–15 nm for Na-, Al(III)- and Co(II)-montmorillonite. After intercalation, these values increased

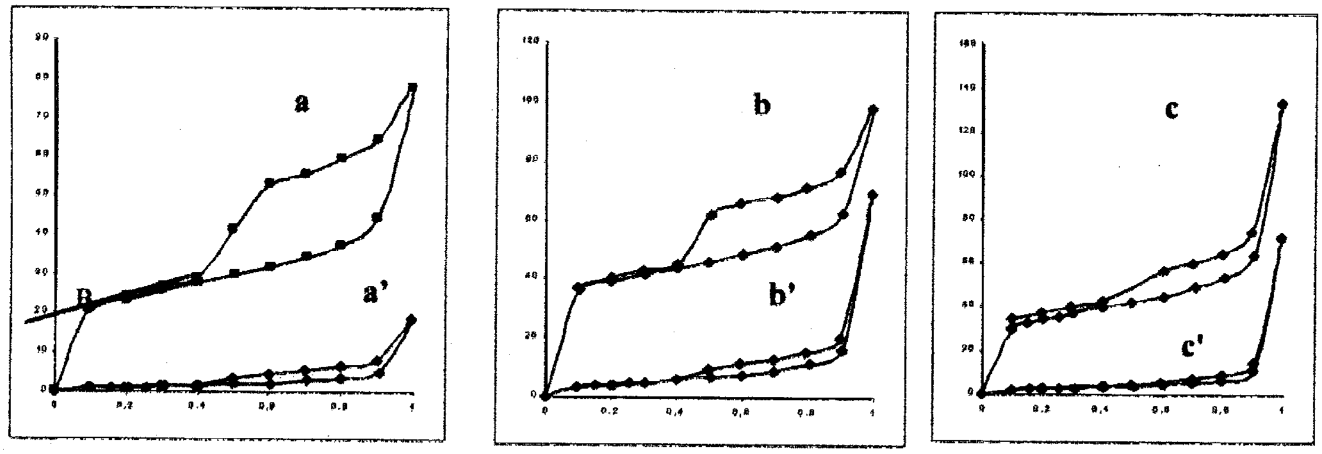

Figure 5. Adsorption and desorption isotherm for (a) Na-mont, (a') 2Mpy-Na-mont, (b) Al-mont, (b') 2Mpy-Al-mont, (c) Co-mont and (c') 2Mpy-Co-mont.

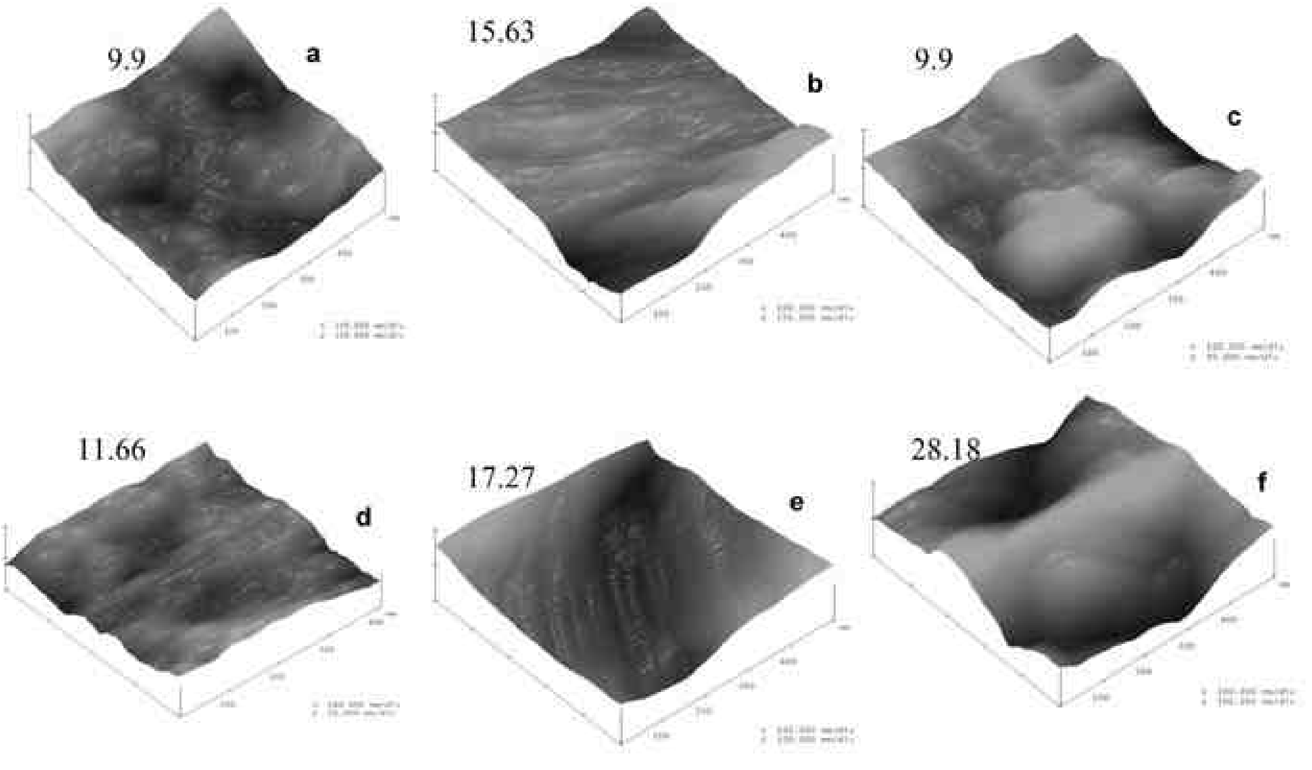

Figure 6. AFM images of (a) Na-mont, (b) Al-mont, (c) Co-mont, (d) intercalated Na-mont, (e) intercalated Al-mont and (f) intercalated Co-mont.

considerably, due to intercalation of bulky compound into the interlayer space of montmorillonite.

3.5 *Molecular arrangement and structure models*

Several authors have studied the coordination chemistry of pyridine thiol–thione (Umakoshi *et al* 1990; Javier Cabeza *et al* 1998; Alonso and Salomo 1999; Jung *et al* 1999; Matthew *et al* 2001; Rafat *et al* 2004). 2-Mercapto-

Table 3. Microspore volume and specific surface.

	Specific surface (m^2/g)	t-Method microspore volume (10^{-2} cc/g)
Na-mont	77·38	2·083
Intercalated Na-mont	4·26	0
Co-mont	111·11	1·89
Intercalated Co-mont	9·38	0
Al-mont	122·5	3·19
Intercalated Al-mont	15·7	0

pyridine can act both as thione and as thiolate ligand to adopt to a variety of coordination modes (figure 7). In our case, we have studied Co(II). The complexes of Co(III) with 2-mercaptopyridine have been reported to form an octahedral structure with two thione molecules and only one thiol (Jung *et al* 1999). It is well known that two Co(III) and Co(II) form octahedral complex structure. From FTIR study, we have found that for Al and Co intercalated compounds the peaks of the thiol form predominates over the thione peaks, therefore, we can suppose that there are two thiol molecules and only one thione molecule around the Al(III) and Co(II) cations. From these results, we can postulate various molecular models to explain the interaction of 2Mpy with Na-, Al(III)- and Co(II)-mont and this is shown in figure 8.

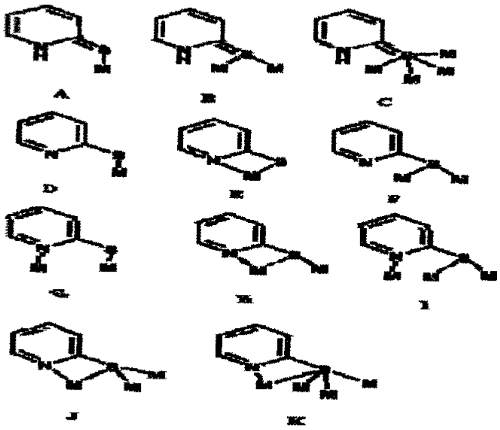

Figure 7. Coordination modes of pyridine thiol–thione with different M metal cations.

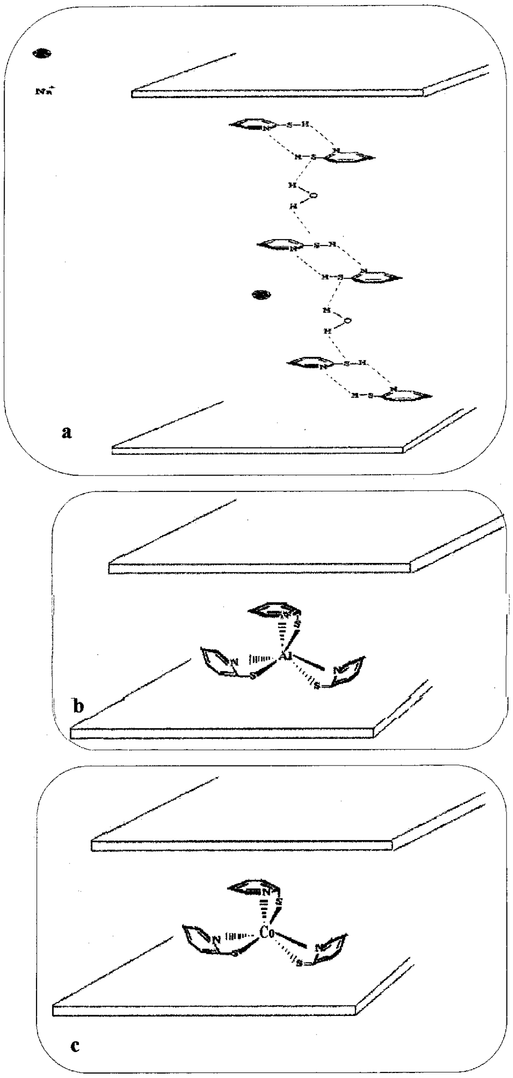

Figure 8. Schematic summary of proposed molecular models in the interaction of 2Mpy with a. Na-montmorillonite, b. Al(II)-montmorillonite and c. Co-montmorillonite.

4. Conclusions

2-Mercaptopyridine molecules were successfully intercalated into the interlayer spaces of sodium, cobalt(II)-, aluminium(III)-montmorillonites by solid–solid reactions. The intercalated molecules of 2Mpy are thought to form coordinating compound in the interlayer spaces of Al- and Co-montmorillonites. However, they are linked through hydrogen bindings in the case of Na-mont.

The tautomeric predominance species present in the intercalation medium depends on the nature of cation, for aluminium(III) and cobalt(II), the two tautomeric forms coexist with slight predominance of the thiol tautomeric form, however, for sodium, only the thiol form coexists. In all cases, an almost total blockage of the interlayer porosity of the clays is done by the organic molecules and the intercalation is accompanied by an increase of the surface roughness.

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